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On the suitability of baked clay for archaeomagnetic studies as deduced from detailed rock-magnetic studies

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SUMMARY

Extensive rock-magnetic investigations have been carried out on baked clays from four kilns (two from Bulgaria and two from Switzerland) found in archaeological sites of different age. Knowledge of the magnetic characteristics of the grains responsible for the archaeomagnetic signal enables us to determine which baked clays have the stablest magnetization and why this is so. This is important in directional studies, but even more so in painstaking palaeointensity studies that require a very careful evaluation of the suitability of the burnt clay material. The proposed rock-magnetic experiments enable the identification of the carriers responsible for the remanence and an adequate interpretation of the experimental results connected with the palaeointensity evaluation. The experimental methods employed are illustrated with the particular results obtained from each of the four kilns studied. The preliminary elucidation of the magnetic mineralogy of the archaeological samples helps first by obtaining a more reliable palaeointensity result, and secondly by explaining some of the discrepancies in the palaeodirectional results. Examples of successful and failed palaeointensity experiments are given in relation to the magnetic properties previously established for each oven. The burnt-clay materials in this present study satisfy the essential condition of carrying a thermoremanence. In spite of that, it is shown that there are many factors that can produce undesirable magnetic properties and thus restrict the suitability of these materials for archaeomagnetic analysis. The most important factors influencing the magnetic behaviour during magneto-diagnostic experiments are: the degree of heating in antiquity, the initial composition of the unbaked material and the burial conditions. The large difference in heating temperatures within a particular archaeological feature is a major cause of variation in magnetic behaviour amongst individual specimens, and so preventing a successful pre-selection of specimens for palaeointensity experiments. Nevertheless, the study has shown a very good coincidence between the determined rock-magnetic characteristics and the success rate in palaeointensity evaluation.

Key words: archaeomagnetism, magneto-diagnostic methods, rock magnetism, suitability for archaeomagnetism.

INTRODUCTION

The main objective of archaeomagnetic studies is to retrace as precisely as possible the variation of the geomagnetic field during the archaeological past. The geomagnetic field direction is defined by its declination and inclination, and its intensity by the magnitude F_a of the field vector. The accumulation of directional results from different parts of the world has progressed much more rapidly than that of absolute field values, although the former requires specially oriented samples. The main reason for this difference is that many methodological difficulties are encountered in palaeointensity evaluations in comparison with directional studies. Indeed, many obstacles must be overcome during experimental intensity determinations (Thellier & Thellier 1959), in many cases preventing a reliable result from being obtained, not to mention that the analyses are very time consuming. For these reasons, the most difficult geomagnetic field element to be determined using dated archaeological baked clays still remains the absolute value of the field. It is well known (Thellier & Thellier 1959) that there are three basic requirements for baked clay concerning its suitability for palaeointensity evaluation. First, that the baked clay *must* carry its original thermoremanence; secondly, that the main carriers are in a single domain state; and thirdly, that the magnetic mineralogy remains unchanged during laboratory heating. Obviously in practice, not all of these requirements are strictly fulfilled, so that the difficulties encountered in palaeointensity evaluation are not surprising.

The aim of this study was to look in detail at the rock-magnetic properties of the baked clay from different kilns in order to evaluate its archaeomagnetic suitability, especially for palaeointensity determination. Despite many previous efforts by other groups there is no unambiguous set of criteria for the pre-selection of suitable samples and this is why in our study we have tried to further enhance our understanding of the rock-magnetic properties of burnt clays. At the same time the acquired experience enables those samples with clearly poor magnetic properties to be rejected, with a consequent economy in laboratory time.

Directional studies, and palaeointensity studies, require a very careful evaluation of the suitability of the burnt clay material. Knowledge of the magnetic characteristics of the particles carrying the archaeomagnetic signal enables us to determine which baked clays have the most stable magnetization and why this is so. The proposed rock-magnetic experiments enable the identification of the carriers responsible for the remanence and an adequate interpretation of the so-called Arai diagram (Nagata *et al.* 1963) during the Thellier experiment (Thellier & Thellier 1959). The accumulated experience of the palaeomagnetic laboratories in Geneva and Sofia (Hedley & Wagner 1982, 1991; Veitch *et al.* 1984; Kovacheva & Toshkov 1994; Jordanova 1996; Jordanova *et al.* 1997; Kovacheva *et al.* 1998; Hedley 2001; Kovacheva & Jordanova 2001) was used as a basis for improving our knowledge of the rock-magnetic properties and the suitability of baked clay for archaeomagnetic analysis.

1 MATERIALS STUDIED

Rock-magnetic studies on four archaeological sites (two in Bulgaria and two in Switzerland) have been undertaken.

(1) Two kilns producing domestic ceramics, in the Early Byzantine Christian centre of Serdica ($\varphi = 42.7°$N and $\lambda = 23.2°$E) and now a quarter of present-day Sofia, were sampled yielding 32 independently oriented samples. From these samples 274 specimens were cut for different laboratory analyses. The site is dated from coin finds to the reign of Emperor Justinian II (565–578 AD).

(2) A Thracian kiln discovered during road construction near the town of Gotze Delchev ($\varphi = 41.5°$N and $\lambda = 23.7°$E) enabled five non-oriented pieces of baked clay to be recovered. From them 20 specimens were cut for detailed rock-magnetic and palaeointensity analyses. Archaeological evidence indicates an age for the kiln between the eighth and seventh century BC.

(3) Six non-oriented pieces of well-burnt clay from the kiln of a potter at Reinach (Basel-Landschaft, BL, Switzerland) ($\varphi = 47.5°$N and $\lambda = 7.6°$E) were used to prepare 22 specimens. This structure, which has been the subject of a directional study of the ancient geomagnetic field in the Geneva laboratory (Hedley 2002a), has also been investigated for its rock-magnetic properties and for palaeointensity determination. The archaeological date lies between the seventh and eighth century AD.

(4) Four non-oriented pieces of baked clay were taken from the kiln of a potter discovered in Voltastrasse (Basel city, BS) ($\varphi = 47.6°$N and $\lambda = 7.6°$E). In all, 14 specimens were cut from them for different laboratory analyses including the Thellier palaeointensity experiment. The archaeological evidence indicates a late Iron Age date between the second and the first century BC.

2 EXPERIMENTAL METHODS AND RESULTS

The remanence of the baked clay specimens was measured using three different magnetometers: two spinner magnetometers, JR-4, (Agico, Brno) and Minispin (Molspin, Newcastle upon Tyne) and one astatic magnetometer AST (Boroc, Russia). Laboratory isothermal remanence (IRM) was induced in a pulse magnetizer made by the Sofia laboratory with a maximum field of 2 T. Zero-field thermal demagnetization was carried out in a shielded oven, also constructed by the palaeomagnetic laboratory in Sofia. A small magnetically shielded oven (Boroc, Russia) was used for continuous thermal demagnetization of the natural remanent magnetization (NRM) and laboratory-induced IRM. Room-temperature magnetic susceptibility was monitored during thermal treatments using a KLY-1 or KLY-2 kappa-bridge (Agico, Brno). The frequency dependent susceptibility was measured with a Bartington (Oxford) MS2 susceptibility meter using a *B* probe. Curie temperatures were determined in a high-temperature attachment of the KLY-2 kappa-bridge (AGICO, Brno). The palaeointensity experiments were carried out in the ambient geomagnetic field using two non-magnetic ovens (Sofia laboratory), whilst an AF demagnetizer with tumbler (Molspin, Newcastle upon Tyne) was used for stepwise AF demagnetization.

In order to improve our knowledge of the nature of the magnetic carriers present in the samples, their domain state, stability, and in general their suitability for archaeomagnetic studies, different laboratory analyses have been carried out.

(1) Magnetic viscosity was evaluated by keeping the samples in a field-free space for 3 weeks following the initial remanence measurement, NRM_0. This test is known as the 'zero-field cleaning' method. The viscosity coefficient S_v was then calculated according to the relation $S_v = [(NRM_0 - NRM_{st})/NRM_0] \times 100$. The stable component ($NRM_{st}$) corresponds to the second remanence measurement after the zero-field storage. The method was applied to 330 specimens from the four sites. The majority of samples have S_v values of between 1 and 5 per cent (Fig. 1).

(2) Stability against alternating field demagnetization was analysed on 25 pilot specimens from all the collections. It is also indicative of the kind of ferrimagnetic minerals present in the material, through the coercivity of the ferrimagnetic grains. Low values of the median destructive field (MDF) show the presence of magnetite and/or an unstable viscous component, while high values point to the presence of iron oxyhydroxides (mainly goethite) or of haematite. The MDF is the AF value, at which half of the NRM is randomized (Dunlop & Ozdemir 1997). The histogram in Fig. 2 shows that the MDF values vary between 8 and 40 mT. The average MDF values for each site are: Serdica, 22 mT; Gotze Delchev, 13 mT; Reinach, 20 mT and Voltastrasse, 25 mT.

(3) The domain state of the ferrimagnetic carriers has been investigated by applying the Lowrie–Fuller test (Lowrie & Fuller 1971) on 25 pilot specimens from the four collections. The method is based on the different stability against AF demagnetization of single- (SD) and multidomain (MD) assemblages of magnetite grains magnetized in magnetic fields of different strength. The NRM carried by the baked clay samples is produced in a weak geomagnetic field, whereas the laboratory IRM is induced in a strong magnetic field. The relative trend of the two decay curves during AF demagnetization determines the type of predominant carriers in the sample studied. In spite of some criticism of this method by Xu &

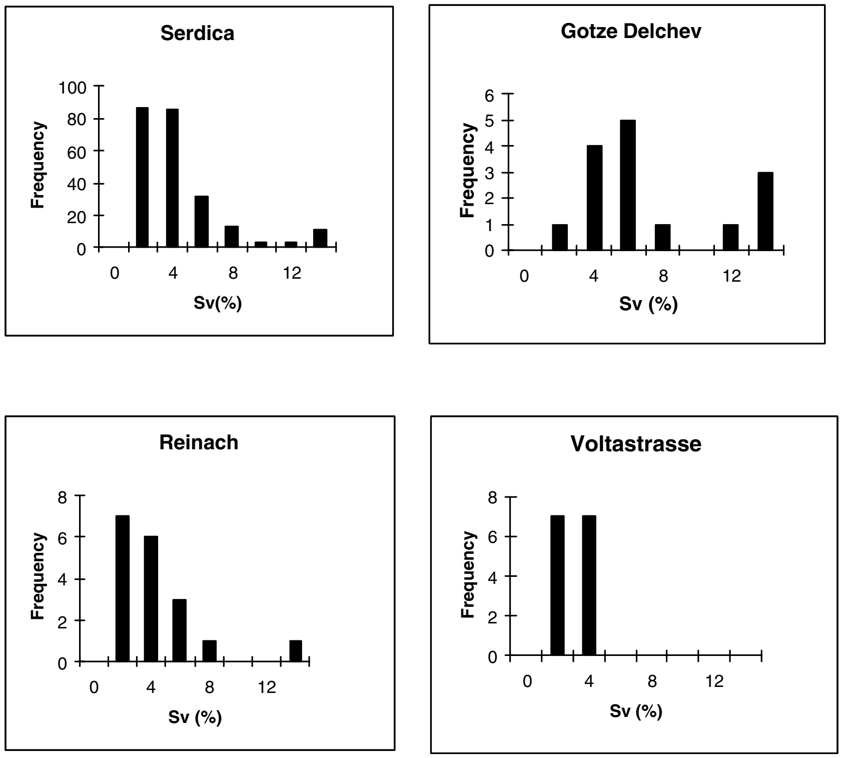

Figure 1. Histograms of viscosity coefficients S_{v} obtained for the different sites.

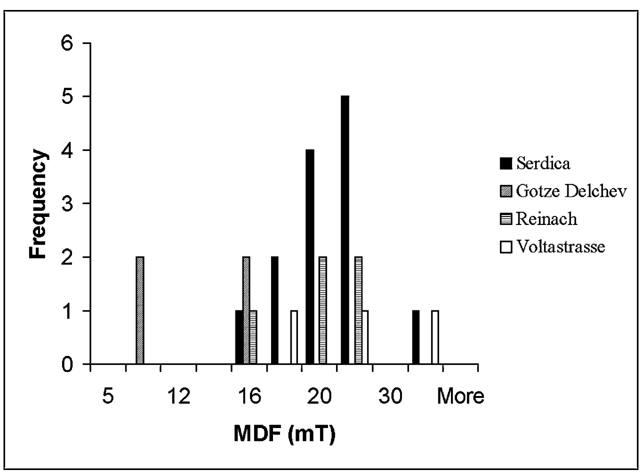

Figure 2. Histograms of median destructive fields (MDF) obtained for materials of different sites.

Dunlop (1995), we consider that when dealing with materials of similar origin the test may be a useful indicator of relative grain size and hence of palaeomagnetic stability. The parameter $\Delta H_{1/2}/H_{1/2} = (\mathrm{MDF_{NRM}} - \mathrm{MDF_{IRM}})/\ \mathrm{MDF_{NRM}}$, defined by Dunlop (1983), has been calculated for discriminating between SD-type behaviour, and pronounced SD-type configuration called 'bi-modal', 'mixed' and MD. Examples from the different sites are shown in Fig. 3.

(4) The magnetic carriers present in the baked clay were determined following two different techniques: thermal demagnetization of a laboratory-induced three-axes isothermal remanence (3IRM) using three different magnetic field strengths (Lowrie 1990) and by the high-temperature behaviour of magnetic susceptibility $K(T)$. In Fig. 4 some representative examples are given of the first method (3IRM), which was applied to 30 specimens. Fig. 5 shows some examples of $K(T)$ behaviour from 31 crushed specimens. The parallel determination of unblocking temperatures, made by continuous demagnetization of saturation remanence (J_{rs}) has been performed on samples from one of the sites (Serdica). This analysis consists of the continuous recording of two successive thermal demagnetizations of the same specimen after saturation in a steady field of 2 T. In Fig. 6 two examples are given. The unblocking temperatures seen on the first demagnetization curves (J_{rs1}) are in a low-temperature range and those below 100°C correspond to the unblocking of secondary iron oxyhydroxide (goethite). The higher unblocking temperatures (around 150–200°C), could be linked to the presence of haemoilmenites, considering that they persist in the second demagnetization curves (Pecherskij *et al.* 1975). The ratio $J_{\mathrm{rs2}}/J_{\mathrm{rs1}}$, calculated from the J_{rs} values measured after the initial saturation and after the second saturation of the already heated samples, respectively, is used to detect whether changes have occurred in the sample during heating. This parameter varies widely for the samples studied and depends on the particular mineralogy, and indirectly, on the degree of firing of the corresponding material. The histogram of $J_{\mathrm{rs2}}/J_{\mathrm{rs1}}$ ratios for the Serdica samples is given in Fig. 7.

(5) Magnetic mineral stability during laboratory heating is a very important condition for reliable palaeointensity determinations and therefore monitoring eventual chemical/phase changes during heating is necessary. The method of Van Velzen & Zijderveld (1992) has been simplified in order to be less time consuming (Jordanova 1996; Jordanova *et al.* 1997). The modified method is based on the subsequent saturation of a specimen in a field of 2 T after each temperature step, measurement of the magnetic susceptibility, of $\mathrm{SIRM_{left}}$ and of the newly produced SIRM. The coercivity spectra of $\mathrm{SIRM_{left}}$ and SIRM were not investigated as proposed in the original method of Van Velzen & Zijderveld (1992). The thermal decay curve of $\mathrm{SIRM_{left}}$ is compared with the thermal decay curve of a

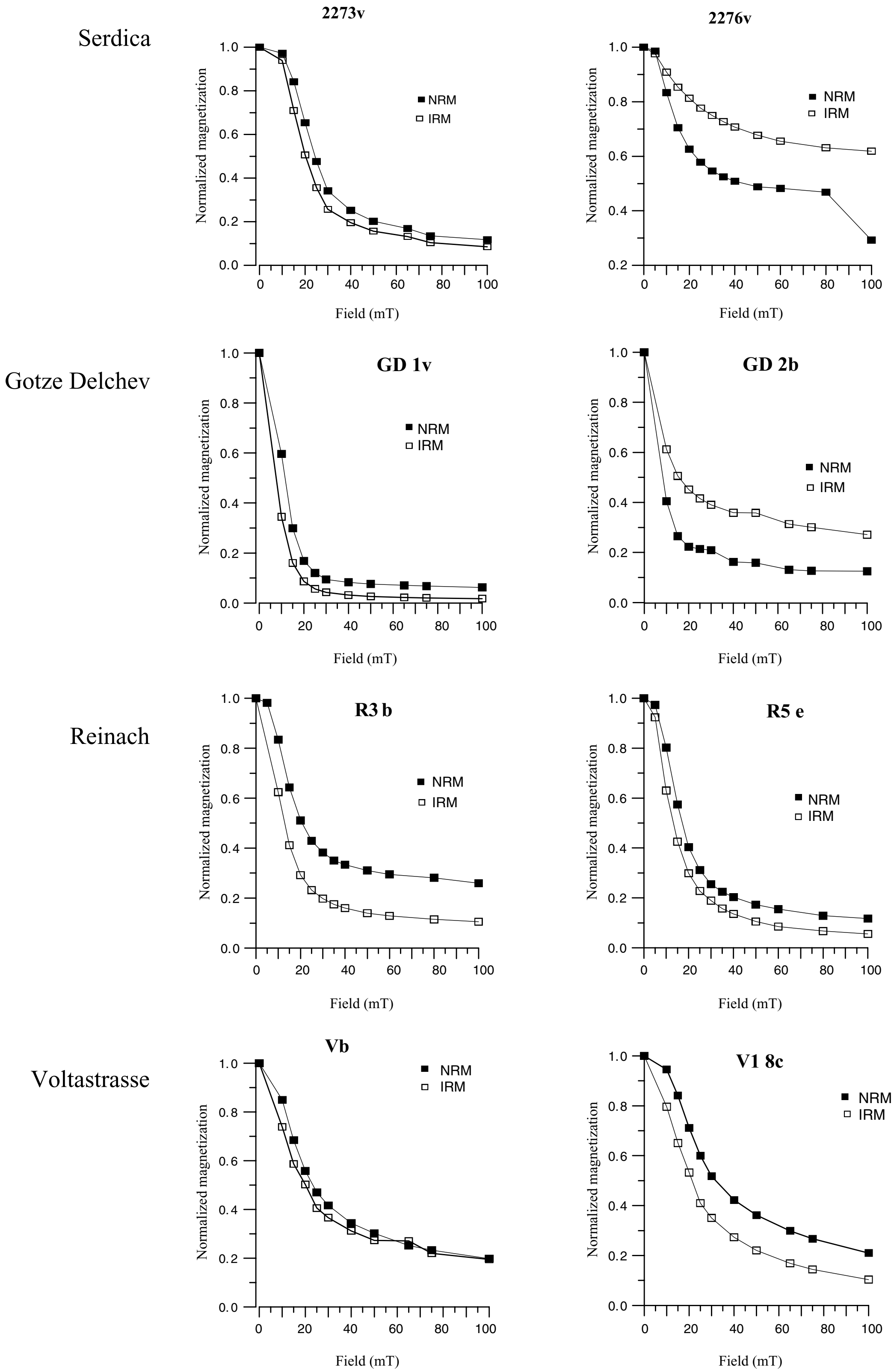

Figure 3. Examples of Lowrie & Fuller (1971) test, performed on samples from the studied sites.

sister specimen that has been saturated only once before the heating procedure. Usually the modulus of three-axes IRM, denoted by 3IRM and performed on this sister specimen, is used. The thermal decay of 3IRM(T) reflects the initial mineralogy of the sample, while $\mathrm{SIRM_{left}}(T)$ also contains the saturation remanence of the newly formed magnetic phases with T_c being higher than the corresponding temperature step. Coincidence of the two SIRM(T) decay curves and stable behaviour of SIRM(2 T) indicate that during each

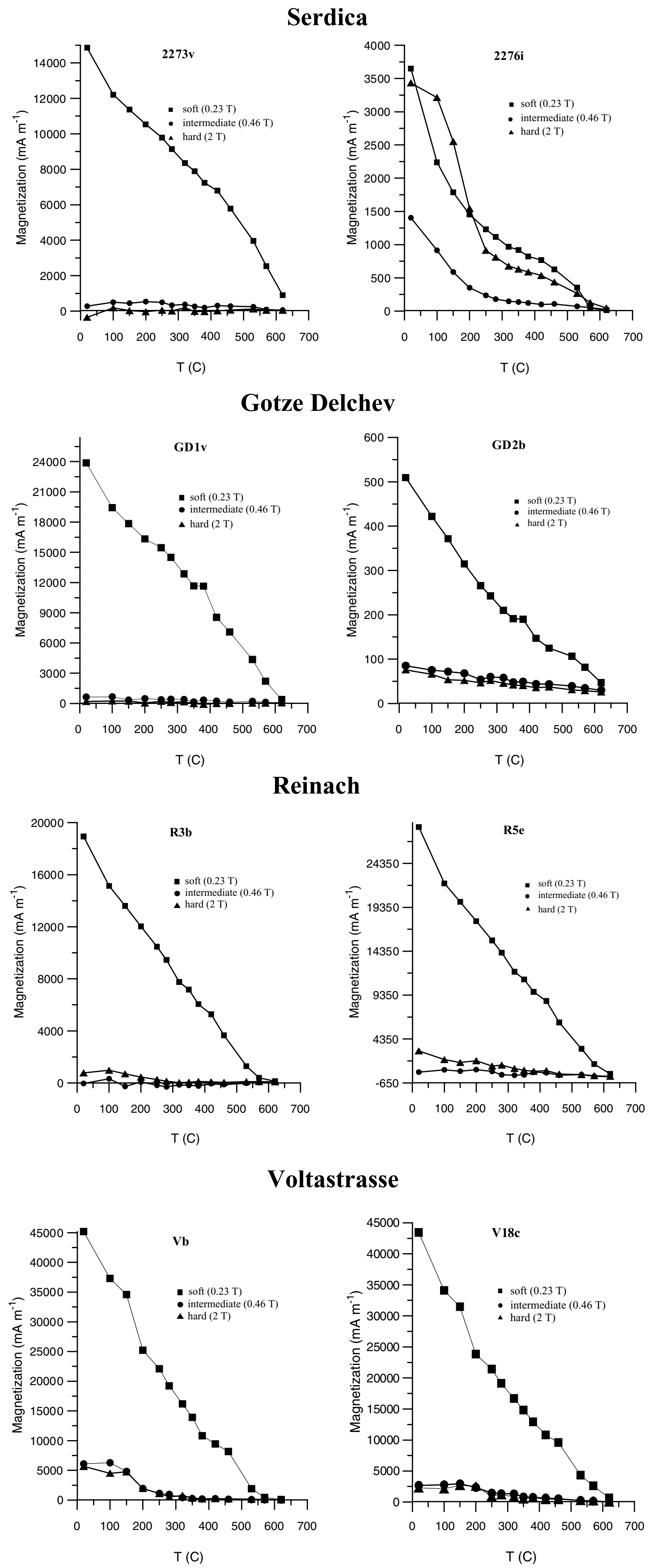

Figure 4. Examples of laboratory-induced three-axes IRM thermal demagnetization (Lowrie 1990).

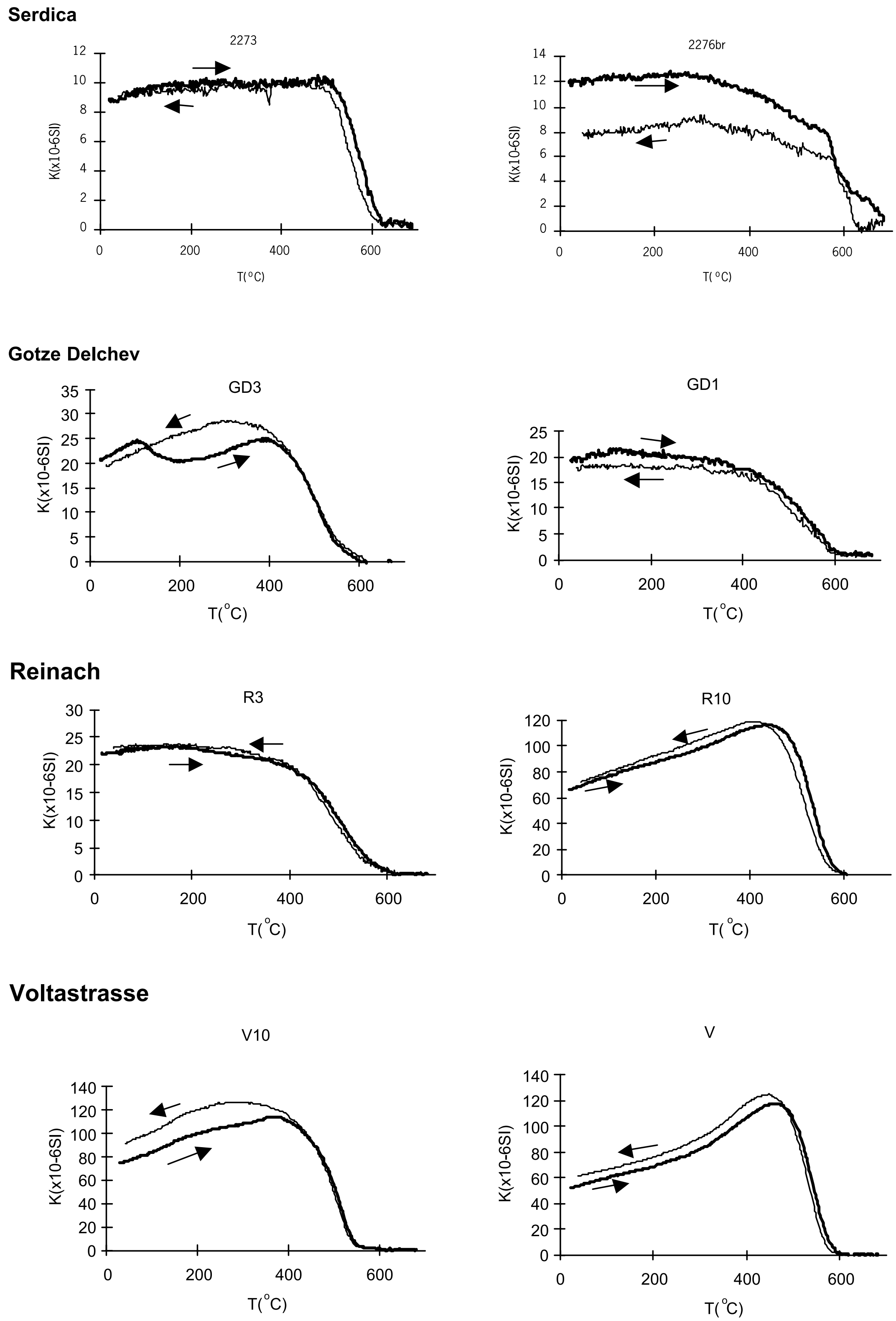

Figure 5. High-temperature susceptibility behaviour.

successive heating no new ferrimagnetic phase, capable of carrying remanence, has been produced. Examples from the four sites are given in Fig. 8.

(6) Frequency dependence of the magnetic susceptibility. It is well known (Dearing *et al.* 1996; Worm 1998) that the finest superparamagnetic (SP) magnetite grains (sizes 0.01–0.02 μm) exhibit higher values of initial magnetic susceptibility when measured in a field of a lower frequency. Frequency-dependent susceptibility measurements on archaeomagnetic samples studied by Jordanova *et al.* (2001) suggest that all baked clay materials contain a

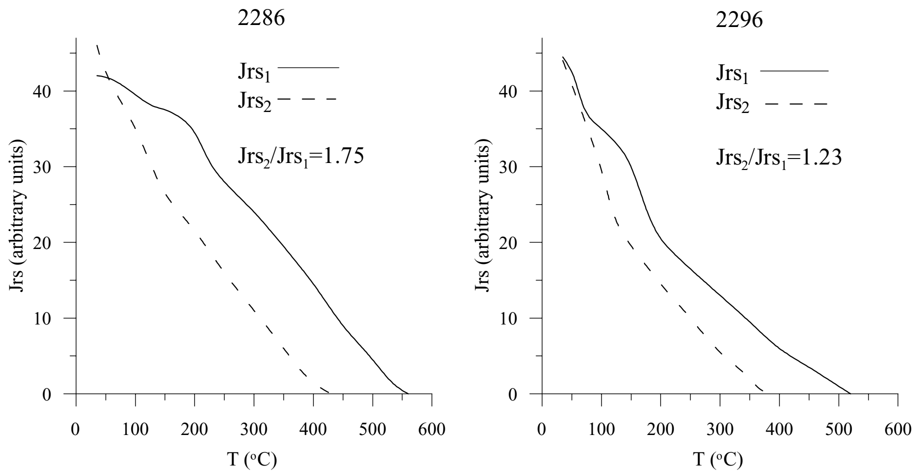

Figure 6. Continuous thermal demagnetization of saturation remanence (J_{rs}) performed twice on the same specimen.

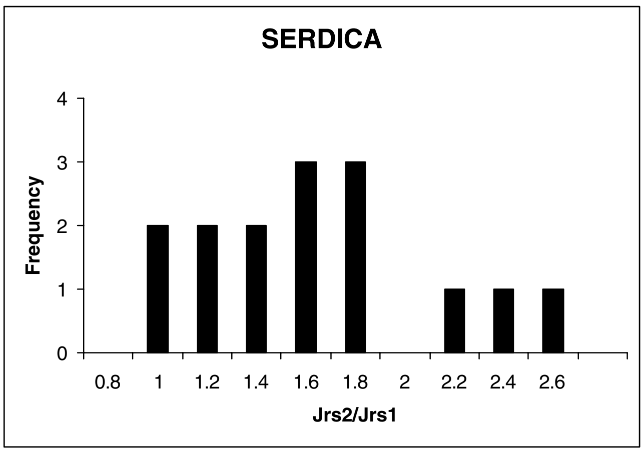

Figure 7. Histogram of ratios J_{rs2}/J_{rs1} for studied specimens from the Serdica site.

significant amount of fine SP grains. The samples from the above studies give values of percentage frequency-dependent susceptibility χ_{FD} (defined as $(\chi_{LF} - \chi_{HF}) \times 100$ per cent$/\chi_{LF}$) varying between 5 and 12 per cent. From the four collections of the present study 88 specimens were measured and the histogram of the values of χ_{FD} (per cent) is displayed in Fig. 9. The distribution shows that χ_{FD} covers the same range ($5 < \chi_{FD} < 14$ per cent) with a maximum at 10 per cent. This, according to Dearing *et al.* (1996) corresponds to 20–50 per cent and even a greater percentage content of fine SP grains in the material. The high values of χ_{FD} prove the presence of a considerable fraction of fine particles in the superparamagnetic state, resulting from different processes related to transformations of the clay matrix during multiple original firings (Jordanova *et al.* 2001).

(7) Anisotropy of the remanent magnetization. The remanence anisotropy in different archaeological materials used in archaeomagnetism can bias the final direction results (Lanos 1987) and intensity determinations (Aitken *et al.* 1981; Garcia *et al.* 1997; Chauvin *et al.* 2000). Previous studies have demonstrated that the anisotropy effect on the palaeointensity determination is greatest in pottery samples (Jordanova *et al.* 1995; Genevey & Gallet 2002; Chauvin *et al.* in preparation). In spite of the fact that the materials in our study are neither pottery nor brick fragments (with the exception of three samples), we have investigated the remanence anisotropy of the samples used for palaeointensity determination. It has been shown that the anisotropy of a laboratory-imparted anhysteretic remanent magnetization (ARM) is a good approximation of the TRM anisotropy (Stephenson *et al.* 1986; Selkin *et al.* 2000; Hus *et al.* 2002). The degree of remanence anisotropy obtained for the 26 samples studied varies between $1.03 < P' < 1.28$ except in a few cases with higher values, up to 1.58. This relatively important anisotropy leads to small correction factors 'f' for the palaeointensity evaluation of the material from the four collections studied. In general, the factor 'f' varies between $0.96 < f < 1.05$ and only in three cases does it reach 12 per cent. This surprising result calls for an explanation and a proposal has been formulated by Chauvin *et al.* (in preparation).

A summary of the rock-magnetic characteristics of samples from the different sites is presented in Table 1. The largest collection is from Serdica, while the other three sites yielded more limited material, because additional specimens were needed for palaeointensity determination, excluding detailed rock-magnetic experiments.

3 ROCK-MAGNETIC CHARACTERISATION OF THE STUDIED SITES

A summary of the magnetic properties studied is given below.

Site Serdica. The baked clays from Serdica (Table 1) are characterized by a predominantly bi-modal behaviour in the Lowrie–Fuller test, typical of non-selected clay used for the construction of ovens to produce domestic wares. There are two samples in this collection (2275 and 2276) that come from bricks used in the construction of the oven. In addition to the expected two-component remanence carried by them (in the case of insufficient reheating), these two samples demonstrate an apparent MD-like behaviour (e.g. IRM is more stable than NRM upon AF demagnetization; Fig. 3). In our opinion this should be linked to the presence of a high coercivity fraction, which contributes to IRM, but not to NRM. This assumption is strongly supported by the result of the three-axes IRM thermal demagnetization (Fig. 4). In fact, it is important to bear in mind that the Lowrie–Fuller test assumes that the NRM is carried by magnetite, so that if other high-coercivity mineral phases such as haematite and goethite are present, the results will be biased. The same brick samples show the highest MDF values (Table 1 and Fig. 2) with 20–40 per

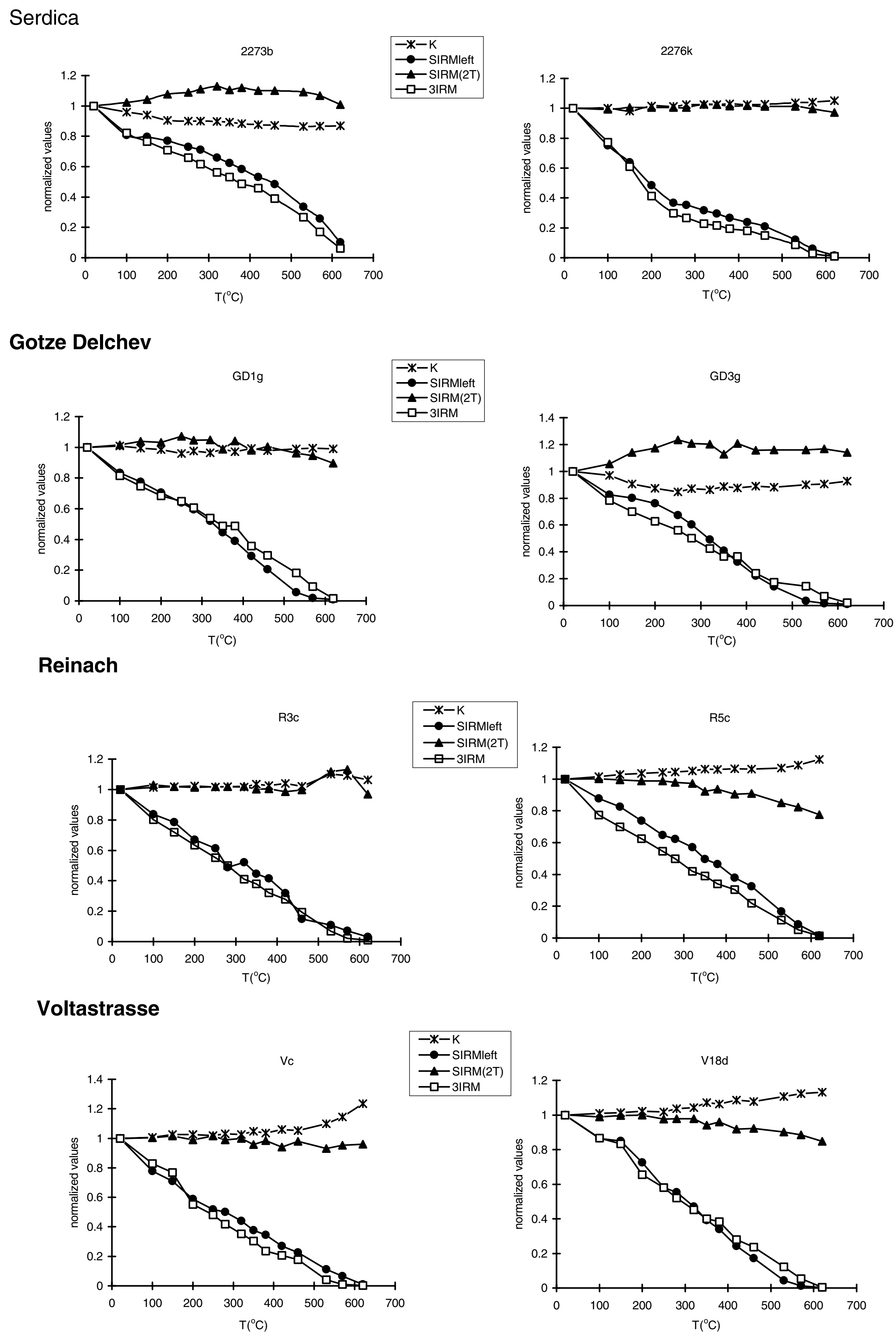

Figure 8. Examples of experiment, applied to detect chemical/phase changes during heating.

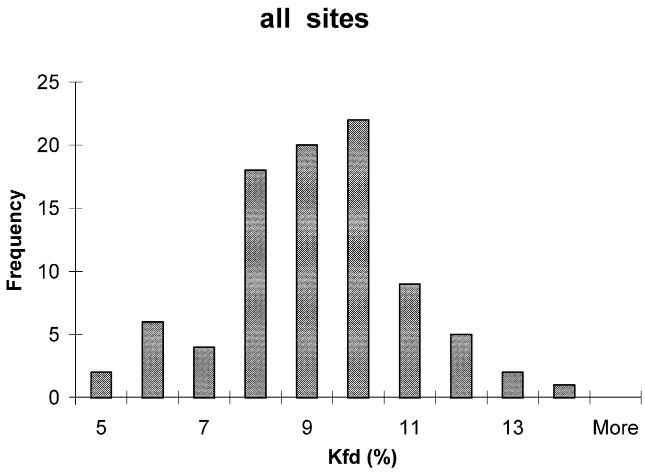

Figure 9. Histogram of the measured K_{fd} per cent of 88 specimens from the four studied sites.

cent NRM remaining after applying 100 mT AF. In contrast to the brick samples the other samples have an MDF of the order of ∼20–25 mT and low NRM left after AF demagnetization at 100 mT, but showing good stability against AFs. They probably contain stable SD/PSD (pseudo-single domain) magnetite/titanomagnetite grains (see also the last column of Table 1). Sample 2273v from Serdica in Fig. 4 confirms the results from AF demagnetization, showing that the baked clay contains mainly magnetically soft minerals. Since the maximum T_{ub} of the soft component is approximately 620 °C, we assume the presence of oxidized magnetite (maghemite). If this oxidized magnetite is in a form that does not invert to haematite (Dunlop & Ozdemir 1997) and appears as a primary mineral, then it is a favourable sign for the suitability of this material for archaeomagnetic studies.

The maximum of the S_{v} histogram lies between 2 and 6 per cent (Fig. 1), suggesting that the material is generally suitable for archaeomagnetic studies. Nevertheless, there are a few samples with much higher S_{v} values, coming from insufficiently burnt parts of the oven. This is confirmed by the $J_{\text{rs2}}/J_{\text{rs1}}$ ratios being mostly higher than 1 (Fig. 7), which leads to the conclusion that the clay material did not undergo such high temperatures when fired in antiquity. Taking into consideration the evidence for the presence of goethite (the penultimate and last columns in Table 1), problems related to mineralogical stability during palaeointensity evaluation are to be expected. This instability upon heating is best revealed in the SIRM test, during which changes in magnetic mineralogy with temperature occur in most of the cases (Table 1 and Fig. 8; 2273b). This is expressed through the difference between $\text{SIRM}_{\text{left}}$ and 3IRM curves and also by the change in SIRM(2 T). On the basis of this experiment some samples have been rejected for the palaeointensity evaluation (e.g. 2285). From 16 Thellier experiments, the results of 10 experiments have been accepted (examples are shown in Fig. 10). It appeared for this site, that usually samples, which show BM-like behaviour (L–F test) in combination with low unblocking temperatures in the soft component (3IRM experiment) failed to give a successful palaeointensity result.

Site Gotze Delchev. This represents the oldest site studied here and as mentioned previously shows a less stable remanence, obviously caused by insufficient heating. The frequent occurrence of BM-type behaviour, as in other sites, is to be expected and proves the presence of coarse grains in non-selected clay. The predominant magnetically soft carrier is highly oxidized magnetite (Fig. 4 and Table 1). One sample from this site, GD2b (Fig. 3) shows the same apparent MD-like behaviour, caused by a high coercivity fraction, but here in a smaller proportion (Fig. 4) in comparison with the sample 2276v from the Serdica site. The low-temperature unblocking hard component (Table 1; 3IRM and Fig. 5) suggests the presence of secondary goethite formed during burial. For instance, sample GD1g shows a stable mineralogy during heating (Fig. 8), whereas sample GD3g changes considerably. The SIRM test (Fig. 8), in fact confirms the behaviour seen in $K(T)$ (Fig. 5), pointing to the presence of an important fraction of iron oxyhydroxide. The latter obviously transforms into haematite, giving an increase in the $\text{SIRM}_{\text{left}}$ curve in comparison with the 3IRM curve (Fig. 8, sample GD3g). At the same time the newly formed phase produces the increase seen in SIRM(2 T).

The material of this site should be used with great caution for palaeointensity determination. In fact, from nine Thellier experiments the results from only three can be accepted (one rejected experiment is shown in Fig. 10). This is the worst success rate in palaeointensity evaluation among the four sites studied.

Site Reinach. In general, samples of the Reinach site carry a stable remanence (Fig. 1) with a maximum in the MDF spectra (Fig. 2) of between 16 and 24 mT, and in most cases with a considerable residual NRM at 100 mT AF demagnetization. The main carrier is magnetite (last column in Table 1 and Fig. 4) with evidence of low-temperature unblocking of the hard component in the three-axes IRM experiment (penultimate column in Table 1 and Fig. 4). The presence of goethite witnessed in the three-axes IRM (Fig. 4) is at a lower concentration and the SIRM test shows better stability during heating (Fig. 8). The predominantly reversible curve in the high-temperature susceptibility measurements (Fig. 5) is a good indicator of the suitability for archaeomagnetic studies. From the predominant BM behaviour (fifth column in Table 1) we can conclude that the burnt clay from the Reinach site, as for those from the other three collections, contains mainly a mixture of stable SD/PSD grains and coarser particles that is the cause of typical BM behaviour. In contrast to the samples from Serdica, this BM behaviour is not accompanied with low T_{ub} in the soft IRM component (Table 1). One exception is the sample R, from which the palaeointensity result has been rejected. Thus the site can be considered to be suitable for archaeomagnetic studies. In fact, from nine Thellier experiments the results of six have been accepted.

Site Voltastrasse. Of the four collections studied, the burnt clay from the Voltastrasse oven shows the best magnetic behaviour, with the lowest viscosity coefficient (S_{v}) and highest MDF (Figs 1 and 2). When the reversible curves of the high-temperature susceptibility behaviour are taken into account (Fig. 5), together with positive SIRM tests (Fig. 8) it appears that this material is quite suitable for archaeomagnetic studies. The predominant carrier is (titano) magnetite (last column, Table 1). The results of five of the six palaeointensity experiments performed were accepted (examples given in Fig. 10).

4 DISCUSSION

The burnt-clay materials included in this study satisfy the essential ‘requirement’ of carrying a TRM. The Koenigsberger Q factor for the four collections (fifth column, Table 1) generally has values greater than 5, implying a thermoremanent origin for the NRM. The viscosity coefficient S_{v} (fourth column of Table 1) correlates negatively with the Q factor as is characteristic for burnt

Table 1. Summary of rock-magnetic results for the Serdica, Gotze Delchev, Reinach and Voltastrasse sites, respectively.

Site country age	Sample	Mate-rial	S_v (per cent)	$Q=$ NRM/KxF	MDF (mT)	$\Delta H_{1/2}/H_{1/2}$ $L-F$	SIRM(T) mineralogical change	T_b(°C) from three IRM analysis for different components			T_c(°C) $K(T)$
								Soft	Median	Hard	
Serdica Bulgaria 565–578 AD											
	2271g	BC	3.3	6			Big change	350, 550	250, 500	250	
	2273	BC	1.1	12	20	0.25, BM	Moderate change	650	–	–	520
	2274	BC	3.9	8	18	0.23, BM	Small change	650	–	–	120, 500
	2275	BR	2.5	7	25	?, MD	No change	200, 560	200, 650	200, >620	580, ? >700
	2276	BR	2.1	15	40	?, MD	Small change	200, 580	200, ?580	200, 620	580, 700
	2277	BC	7.8	3	20	−0.1, MD?					580-secondary
	2277	BR			15	0.2, SD					400, 580, 700
	2278	BC	3.9	5							580
	2280	BC	2.2	13	25	0.33, BM					550
	2282	BC	5.0	6	20	0.40, BM	Small change	100, 600	–	–	
	2283	BC									∼500, wide spectra
	2285	BC	6.9	5	22	−0.88, BM	Big change	300, 620	–	200	
	2290	BC	1.5	13	25	0.20, SD	Moderate change	580	–	150	∼580, weak
	2291	BC	0.2	22	21	0.28, BM	Moderate change	320, 500	∼320	∼320	100, 500–520
	2296	BC	0.7	31	20	0.17, SD	Small change	200, 580	–	–	
	2301	BC	2.8	16	17	0.14, SD	Moderate change	300, 580, 620		–	100, 520
Gotze Delchev Bulgaria 8–7 century BC											
	GD1a	BC	1.9	9.2							480–580
	GD1b	BC	4.3	9.6							
	GD1v	BC	2.7	13.5	15	0.33, BM	Small change	200, 580	–	–	
	GD1g	BC	2.9	12.5							
	GD2a	BC	16.1	1.9							
	GD2b	BC	10.5	2.3	10	−0.75, MD		460, >620	200	150	
	GD3a	BC	4.2	6.8							
	GD3b	BC	4.4	7.5							100, 400–500
	GD3v	BC	4.4	4.2	15	0.33, BM		460, 580	200	200	
	GD3g	BC	3.2	10.9			Big change				
	GD3d	BC	4.9	6.1							
	GD4a	BC	6.7	7.7							200, 580
	GD4b	BC	3.2	11.5	8	0.35, BM		460, 620	150	150	
	GD5v	BC	13.4	9.6	15	0.33, BM		280, 500, 580	150	–	350, 580
	GD5g	BC	11.9	6.7			Big change				
	GD5j	BC	14.6	5.3	15	0.20, SD		280, 500, 620	–	–	
	GD5i	BC	17.5	4.9			Big change				
Reinach Switzerland 7–8 century AD											
	Ra	BC			15	0.20, mixed		550, >620	150	150	Wide spectra
	Rb	BC	5.7								300, 580
	Rc	BC	7.4	2.5			Big change				∼500, wide spectra
	Rd	BC	1.5	6.9				350, 550	–	–	
	Re	BC	5.1	4.9				200, 580	200, ?580	200, 620	
	Rf	BC	3								
	Rg	BC	0.3								
	R3a	BC	2.1	0.7							
	R3b	BC			20	0.35, BM		580	–	200	∼520, wide spectra
	R3c	BC	20.7	9.1			No change				
	R5a	BC	0.9	12.2							
	R5b	BC	2.6	10.5							
	R5c	BC	1.4	17.7			Moderate change				
	R5d	BC	5.1								
	R5e	BC			20	0.22, BM		620	250	∼150	∼580
	R10a	BC			22	0.30, BM		550	–	–	∼520
	R10b	BC	1.0	18.5							
	R10c	BC	0.6	15.5							
	R10d	BC	1.2	20.7	23	0.33, BM		580	–	–	
	R11a	BC	2.8	22.1							∼600, paramagnetic component
	R11b	BC		11.8							
	R17	BC	3.4	6.2							
Voltastrasse Switzerland 2–1 century BC											
	Va	BC	2.4	9.8							
	Vb	BC	2.3	12.2	25	0.20, SD					480
	Vc	BC	2.4	10.4			Small change	200, 350, 530	200	200	

Table 1. (*Continued*.)

Site country age	Sample	Material	S_v (per cent)	$Q =$ NRM/KxF	MDF (mT)	$\Delta H_{1/2}/H_{1/2}$ $L - F$	SIRM(T) mineralogical change	T_b(°C) from three IRM analysis for different components: Soft	Median	Hard	T_c(°C) $K(T)$
	V1b	BC				0.14, SD		330, 580	–	–	620
	V10a	BC	1.9	9.2							~500 wide spectra
	V16a	BC	1.8	6.6							
	V16b	BC	1.9	9							
	V16c	BC	1.9								
	V16d	BC	2.9	9.3	17	0.23, BM	No change	350, 580, 620	250	150	
	V16e	BC	2.1	8.5							
	V16f	BC	1.1								
	V18a	BC	0.4	8.6							500–580
	V18b	BC	2.2	7.8			Small change				
	V18c	BC	0.7	20.8	33	0.27, BM		200, 460, 620	250	250	
	V18d	BC	3.6	16.8							

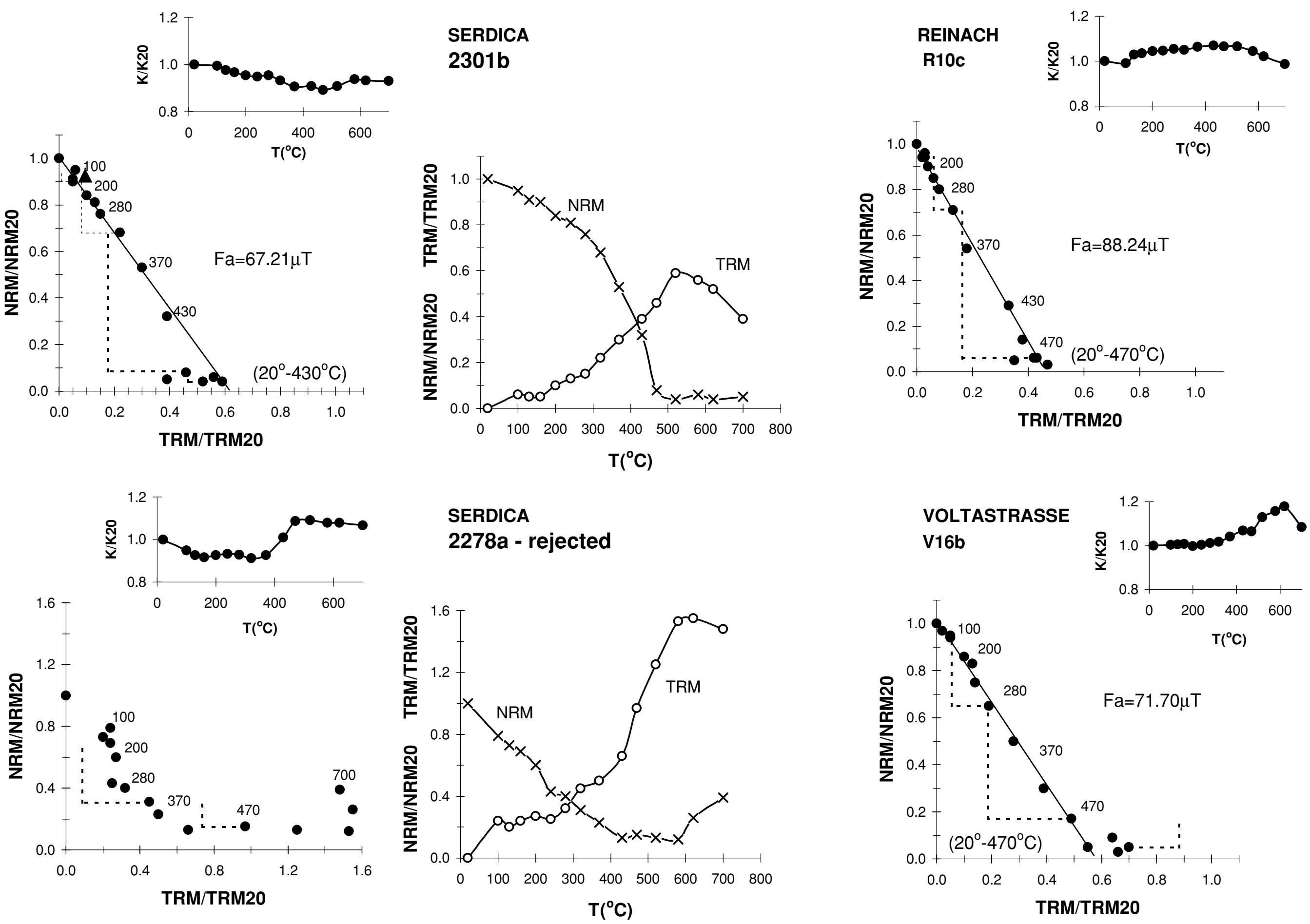

Figure 10. Examples of four successful and two unsuccessful Thellier experiments coming from the study sites. Results are shown with their Arai diagrams (Nagata *et al.* 1963). The dashed lines correspond to the PTRM tests (Thellier & Thellier 1959).

archaeological structures (Hedley, in press). Unfortunately, there are many factors that can produce undesirable magnetic properties and restrict the suitability of these materials for archaeomagnetic analysis. The most important factors influencing the magnetic behaviour during magneto-diagnostic experiments, are given below (Kovacheva & Jordanova 2001).

Degree of heating. In spite of the apparently well-baked appearance of the samples taken, they very often carry only a partial thermoremanence (PTRM), which although sufficient to obtain reliable directional results, are not sufficiently baked for a satisfactory palaeointensity determination. First signs come from the magnetic viscosity evaluation. Fig. 1 suggests that the most strongly burnt material is that from the Voltastrasse kiln. In addition, the same material shows the highest stability against AF demagnetization (Fig. 2). The samples from the Gotze Delchev site are more viscous (Table 1 and Fig. 1) and are magnetically 'very soft' with MDF values smaller than 10 mT for half of them (Fig. 2). It is important to mention that often a large within-sample variation in S_v (e.g. from subsamples of the same piece of material, called specimens) is observed, such as in R3a and R3c (Table 1). It is clear that the 'c' specimen was cut from the part of the sample where heating was less intense. We have previously pointed out (Kovacheva *et al.* 1998) that such large variations in baked clays are caused by non-uniform heating. Insufficiently burnt clay usually demonstrates a poor mineralogical stability during laboratory heating. This can be seen in the histogram of J_{rs2}/J_{rs1} ratios (Fig. 7) of the Serdica collection, where the saturation remanence of specimens increases considerably after the first heating to 700 °C. The great change in remanence acquisition capacity can be caused by the formation of new magnetic phases coming from the clay matrix that was not subjected to high temperatures in ancient times. This leads to the next important factor.

Composition of the initial unbaked material. The fired archaeological structures studied were made from different clays, soils or loams. All of these materials contain mainly phyllosilicate minerals of extremely fine grain size. Strongly magnetic Fe-bearing minerals are present usually as accessory phases. Depending on the type of clay mineral (e.g. kaolinite, montmorillonite, etc.), there are significant differences in the content of Fe ions present as substitutions in the structure of the clay minerals (Cornell & Schwertmann 1996). These cations are potential sources for the creation of strongly magnetic minerals during heating to high temperatures, where a breakdown of the clay minerals occurs (Murad & Wagner 1998). As discussed in Jordanova *et al.* (2001), differences in the dominant clay minerals are one of the reasons for varying magnetic enhancement of burnt clays. There is also an 'anthropogenic' factor, when the raw material has been intentionally pre-selected and prepared for the manufacture of pottery and bricks in ancient times (Kovacheva *et al.* 1998). Consequently, bricks and pottery are in general more homogeneous and fine-grained than materials from ovens and kilns. The baked clays studied here are not made of pre-selected materials. Thus we may expect a large grain-size spectrum, which explains the frequent occurrence of bi-modal behaviour of specimens during the Lowrie & Fuller (1971) test (Table 1). As explained by Dunlop (1983), low field magnetization such as NRM is governed by the fine grains, while high field remanence is influenced by the presence of the coarser grain fraction. Thus, the AF demagnetization curve of IRM is much softer and tends to decay exponentially, which causes a pronounced SD-type configuration called 'bi-modal' (BM). From the 25 pilot specimens examined, 15 demonstrate such a behaviour, proving the existence of both SD fine grains and coarse ones.

The third main factor influencing the magnetic behaviour of baked clay is:

Burial conditions. Before being unearthed the archaeological structures sampled for archaeomagnetic purposes have been buried since they were abandoned. Inevitably they were influenced by environmental conditions, and consequently by weathering. Thus 'primary' materials probably underwent modifications (Weaver 1989). The alteration of wetting/drying and freezing/thawing cycles, and a fluctuating ground water level can cause the formation of secondary magnetic phases such as iron oxyhydroxides (Barbetti *et al.* 1977). The low Curie temperatures (T_c) seen in $K(T)$ curves (last columns in Table 1 and Fig. 5) show that samples from the Gotze Delchev site contain goethite. It is clear that GD3 with a pronounced presence of goethite has been much more influenced by weathering processes than GD1. There is also a difference in the main magnetic carrier if we compare the high-temperature T_c registered by the two specimens from the same structure. Thus, as in the case for the degree of heating, burial conditions do not influence the entire structure in the same way.

Therefore, the observed difference in magnetic behaviour between samples coming from the same site is caused by one or several of the factors discussed above. The method proposed for the detection of mineralogical changes occurring during heating (Jordanova 1996), has the advantage, that it relies on the remanence-acquisition parameter SIRM, while magnetic susceptibility reflects the contribution of all grain sizes and mineral assemblages (including para-, dia- and ferrimagnetic phases). The only drawback to its application is that even this simplified method in comparison with the original one, developed by Van Velzen & Zijderveld (1992) is still time consuming, but on the other hand, it gives much valuable information.

CONCLUSION

The detailed rock-magnetic studies carried out on four collections of baked clays of different age lead to a better understanding of the factors causing the variation in magnetic behaviour of samples during laboratory treatment. These factors, as described above, often lead to unfavourable heterogeneity amongst the samples taken from a given structure. The results obtained here agree with our previous observations (Jordanova 1996; Jordanova *et al.* 1997; Kovacheva *et al.* 1998; Kovacheva & Jordanova 2001). The relation of the rock-magnetic results to the success of the palaeointensity experiments cannot be defined through one simple parameter or characteristic. The presence of weathering products (iron oxyhydroxides) and, of course, multidomain magnetite grains are often a warning as to a possible failure of the palaeointensity experiment, even in cases when no significant mineralogical changes during heating are detected. Thus, the suitability of baked clay for archaeomagnetic studies can only be established by taking into account the results from a series of rock-magnetic experiments as proposed here. From this study a further step in our understanding of the magnetic behaviour of baked clay has been achieved. One can immediately conclude that the site Gotze Delchev that has shown the worst characteristics during the series of rock-magnetic tests is the site with the poorest success rate during the palaeointensity experiment. Conversely, the Voltastrasse site that revealed the best magnetic behaviour also has the highest success rate in palaeointensity evaluation.

The preliminary elucidation of the magnetic mineralogy of the archaeological samples helps in obtaining a more reliable palaeointensity result. The large difference in maximum heating temperatures and in the amount of secondary phase produced by hydration during burial within a particular feature are the major causes of non-uniformity in magnetic behaviour between individual specimens.

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